

Preparation and Properties of Starch Acetate

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SCHUETZENBERGER (15) in 1865 reported the preparation of starch acetates by the action of glacial acetic acid, acetic anhydride, or acetyl chloride on starch. The first commercial process for making starch acetates, patented by Cross and Traquair (7) in 1904, consisted in heating dry starch with less than its weight of glacial acetic acid to produce a water-soluble ester. This product has been marketed under the name of "feculose" and used in tub-sizing of paper (18, 19, 20).

Recently renewed interest in starch acetate has been evidenced by its manufacture by an American company and by publication of recent research (4, 5, 11, 12, 13, 16). Water-soluble starch acetates of low acetyl content may be used as film-forming agents in certain flotation processes (8), in the sizing and coating of textiles and paper, in calico printing, for confectionery fillings and coatings (13), and as addition agents in baking doughs (2).

Highly acetylated starch has been suggested for use in plastics, and its solutions have been proposed as water-resistant adhesives, coatings, and sizes for both porous and nonporous materials. Mullen and Pacsu in a recent publication (12) reviewed the industrial possibilities of starch esters, suggesting in addition to coatings and adhesives their application as diluents for other plastics and their use in compounding soft elastomers and in the form of aqueous emulsions.

Investigators have reported that starch is difficult to acetylate with acetic anhydride under moderate conditions (3, 4). Glacial acetic acid acetylates starch completely but requires long boiling in the acid and results in a degraded product, mainly the result of acetolysis (6).

The use of anhydrous (98 to 100 per cent) formic acid and mixtures of anhydrous formic and glacial acetic acids as patented by Whinfield and Ritchie (22) for swelling starch preparatory to acetylation in acetic anhydride. Fused monochloroacetic acid has also been entered as a swelling agent for starch prior to acetylation (17).

The swelling action of formic acid on starch was investigated by Gottlieb, Caldwell, and Hixon (10). They treated 5 grams of cornstarch with 50 ml. of 90 per cent formic acid, letting the mass stand for 24 hours and recovering the product by precipitating in alcohol, washing, and

Conditions of acetylation of potato starch by two methods have been studied: esterification in a mixture of acetic acid and acetic anhydride and acetylation in acetic anhydride of starch preswelled with formic acid. Perchloric and sulfuric acids were found to be superior among a number of catalysts evaluated.

The acetylation of starch preswelled with formic acid required approximately 1 hour at 95° C., as compared with 9 hours for the first method.

Starch acetates having a wide range of viscosity and with different solubility characteristics were made by diversified conditions of preparation. Owing to the short reaction time, acetyl starch prepared by the second method was only slightly degraded. As a result, this method gave esters of higher viscosity.

By the first method air-dry starch gave acetates of higher viscosity than oven-dried starch of nearly zero moisture content. Oven-dried starch was preferred for use with the second method.

In dilute solutions of organic solvents, starch acetates prepared by the second method had viscosities of the same order as high-viscosity commercial cellulose acetate.

drying. Their results show that a monoformate is produced under these conditions.

Acetylation of starch in a mixture of acetic acid and acetic anhydride has been investigated by Burkhard and Degering (4), who pretreated starch in acetic anhydride and then acetylated in the above mixture, with sulfuric acid as catalyst.

In view of this marked interest in the acetates of starch and the several possibilities for their practical application it was deemed advisable to re-examine some of the methods suggested for preparation of these compounds. Experimental work reported in this paper was concerned with a study of two methods of acetylation of starch: (1) acetylation in a mixture of acetic acid and acetic anhydride, and (2) acetylation in acetic anhydride only of starch preswelled in formic acid. The primary object of this investigation was to find the optimum conditions for these methods, such as temperature, reaction time, composition of acetylation medium, the character and concentration of the catalyst, and moisture content of the starch.

Experimental Procedure

DRYING OF STARCH. Air-dry starch was heated in an oven at 100° C. until constant weight was reached. Such starch is designated as "dry starch" in this paper.

ACETYLATIONS. High-grade domestic potato starch was used in all experiments. Both c.p. grade and technical grade (97 per cent or higher) of acetic anhydride were used. No differences were noted in the reaction or character of the product when the grades were interchanged. The acetic acid, formic acid, and catalysts employed were of the c.p. grade.

Acetylations were carried out in all-glass equipment under controlled conditions. Three-neck flasks with ground-glass joints were fitted with a mercury-seal stirrer in one opening, a reflux condenser in the second, and a glass stopper in the third.

Stirring was provided continuously during esterification. The rate of stirring did not affect the rate of acetylation under the conditions used, provided sufficient agitation was supplied to hold the starch in suspension.

Acetylation of Starch in a Mixture of Acetic Acid and Acetic Anhydride with Catalyst Added (Method I). The starch was added to the acetic anhydride; the acetic acid, containing the catalyst, was immediately added to the suspension of starch in acetic anhydride. This method differs from that of Burkhard and Degering in that the starch was not pretreated in acetic anhydride.

Acetylation of Preswelled Starch (Method II). Dry starch was stirred into formic acid at room temperature. After a short time heat was evolved, and the starch swelled, passing through a viscous gel stage and then changing to a white, crumbly mass. The swelled starch was then mixed with acetic anhydride, and the catalyst was gradually added. After addition of the catalyst, if no steps were taken to cool the mixture, the temperature rose spontaneously to 55° or 60° C. Carbon monoxide, which was formed as a result of decomposition of the formic acid, caused ebullition that was rather violent under some conditions. When all the catalyst was added at once, either a waiting period (one hour unless otherwise indicated) was allowed, during which the flask was cooled in an ice-water bath, or the reaction mixture was warmed gradually from 25° to 95° C. in one hour.

Whinfield and Ritchie (22) used either air-dry or oven-dried starch with 98 to 100 per cent formic acid in their examples. The authors found it simpler to use oven-dried starch and commercial 90 per cent formic acid.

RECOVERY AND PURIFICATION OF PREPARATIONS. Starch acetates were recovered and purified by three methods: precipitation in ice water followed by washing, organic solvent precipitation and washing, and dissolving the excess acetylating agent in toluene, followed by distillation of the solution. The first method has been commonly used in previous work,

and was used in all instances unless otherwise specified. In the second method the starch ester was first precipitated by pouring the reaction mass into ether or petroleum ether. The precipitated starch derivative was then washed with the solvent or treated in a Soxhlet extractor until free from acidity. When toluene was used for purification, it was thoroughly stirred into the reaction mixture, which was then distilled under vacuum to near dryness. This process was repeated twice to give a residue of starch ester practically free from acidity. The purpose of the two latter methods of recovery of starch acetate was to ascertain whether or not a complete precipitation was obtained in water.

All samples for physical and chemical examination were dried first in air and finally in an oven at 100° C. Eberstadt's method of determining total acyl (9) in cellulose esters was used in determining acetyl in starch acetate.

VISCOSITY MEASUREMENTS. Viscosity of pyridine solutions of starch acetate samples was determined by the capillary tube method, using the Fenske modification of the Ostwald pipet. The measurements were made in a constant-temperature bath held at 25° ± 0.1° C., according to A.S.T.M. standard procedure. The concentration of the solutions used was 10 per cent unless otherwise indicated. To convert centistokes into centipoises the following data for densities may be used: 1 per cent solution, 0.9803, and 10 per cent solution, 1.0062.

Discussion of Results

METHOD I. In the preliminary work on acetylating starch, tests were made to determine a desirable acetylating medium, suitable catalysts, and appropriate temperature range.

Acetic acid and acetic anhydride were investigated as the esterifying medium, separately and in various mixtures. Mixtures containing equal parts by weight of acetic acid and acetic anhydride were found to be the best. It was further found that 1 part of starch, 2 parts of acetic acid, and 2 parts of acetic anhydride by weight give a reaction mass of a consistency that

can be handled easily with ordinary laboratory equipment. The reaction temperature selected for most of this work was 95° C. This provided a relatively high reaction rate without causing excessive degradation.

A number of compounds were evaluated as catalysts for esterifying starch in acetic acid-acetic anhydride mixtures. Perchloric acid and sulfuric acid were found to be the most effective under the conditions used; the former was used as catalyst for most of the experiments in acetylating unswelled starch. Phosphoric acid gave fairly rapid acetylation without causing much degradation. Aluminum chloride and hydrochloric acid gave moderate acetylation rates but caused serious degradation.

Table I gives comparative data showing changes accompanying variation of the anhydride-acid ratio, variation of catalyst, and variation of temperature. In certain experiments in which the major portion of the product was insoluble in the reaction medium, the solids were allowed to settle and were then separated from the soluble portion. The soluble portion was more highly acetylated than the insoluble fraction. In experiments in which the product was homogeneous, or nearly so, it was recovered as a whole.

Table II shows the effect of variation of concentration of perchloric acid on the acetylation of starch.

The amount of perchloric acid used ranged from 0.070 to 0.453 gram per 100 grams of starch in a mixture of 1 part of starch, 2 parts of acetic acid, and 2 parts of acetic anhydride by weight. In experiments 1 and 2 only a small amount of the starch acetylated sufficiently to dissolve in the reaction mixture. The catalyst concentration in experiment 3 gave almost complete conversion to the triacetate and at the same time the highest viscosity product. Analysis of the acetate recovered from experiment 4 gave the theoretical percentage acetyl for complete substitution but displayed a decidedly reduced

viscosity in comparison with number 3. Experiments 5 and 6 gave products having characteristics of excessive degradation—low viscosity, dark color, and high acetyl value—indicating perhaps the presence of acetylated dextrans and sugars.

It is concluded that the catalyst concentration used in experiment 3 is the optimum for the accepted reaction mixture.

Another important variable that received consideration in studying the acetylation of starch in the acetic acid-acetic anhydride mixture was the moisture content of the starch. When acetylation is carried out in such a mixture, the residual moisture in the starch may be compensated for by addition of excess anhydride equivalent to the moisture. Experiments were carried out to determine what effect the moisture of starch has on the resultant acetate when the initial anhydride-acid proportion is varied to give a final 1 to 1 ratio after conversion of the excess of acetic anhydride to acid by the moisture of the starch. Table III shows that the same high acetylation was obtained in each experiment using starch of 0 to 20 per cent moisture, when moisture was compensated for by addition of anhydride. The viscosities of solutions of the starch acetates, however, showed considerable differences, for which the authors do not have at present an adequate explanation. The starch used for experiment 1 was dried in an oven at 100° C. to constant weight. The starch used for experiment 5 was prepared by wetting air-dry starch and redrying in air to 20 per cent moisture. Samples of starch used for experiments 2, 3, and 4 were prepared by blending the oven-dried and 20 per cent moisture samples.

Various changes accompany the acetylation of starch, beginning with the

Table I. Effects of Varying Reaction Temperature and Catalyst

(Acetylation of Potato Starch in Glacial Acetic Acid, Acetic Anhydride, and Mixtures. Reaction Time, 9 Hours. 50 Grams of Dry Starch)

EXPT. No.	ACETIC ACID Grams	ACETIC ANHYDRIDE Grams	CATALYST Grams	TEMPERATURE ° C.	ACETYL		WHOLE %	VISCOSITY Centistokes ^a	FINAL REACTION MIXTURE
					Soluble fraction %	Insoluble fraction %			
1	200	None	0.105 HClO ₄ ^b	95	23.6 ^c	3.8 ^d	..	1.5	Mainly undissolved material; soluble portion clear, almost colorless
2	133.3	66.7	0.105 HClO ₄ ^b	95	43.0	27.1	..	4.2	Mainly undissolved material; soluble portion light brown
3	100.0	100.0	0.105 HClO ₄ ^b	95	43.8	62.4	Translucent, viscous, amber-colored liquid
4	66.7	133.3	0.105 HClO ₄ ^b	95	41.9	3.3	..	2.7	Mainly undissolved material; soluble portion clear, almost colorless
5 ^e	None	200.0	0.105 HClO ₄ ^b	95	..	0.4	Entire product insoluble in reaction medium
6	200.0	None	None	95	..	2.3	Product insoluble in reaction medium
7	100.0	100.0	None	95	..	3.8	Product insoluble in reaction medium
8	None	200.0	0.29 H ₂ SO ₄	95	42.0	0.4	Mainly undissolved material; soluble portion clear, dark brown
9	200.0	None	0.29 H ₂ SO ₄	95	39.5	1.7	Small amount of undissolved material; light-brown, almost clear liquid
10	100.0	100.0	0.105 HClO ₄ ^b	75	22.7	..	Brown, mobile liquid containing suspended material
11	100.0	100.0	0.105 HClO ₄ ^b	85	33.9/	..	Similar to No. 10 except lighter color
12	100.0	100.0	1.8 H ₂ PO ₄ ^f	95	36.6	..	White, viscous mass
13	100.0	100.0	0.29 H ₂ SO ₄	95	43.6	69.3	Viscous, amber-colored liquid
14	100.0	100.0	2.0 AlCl ₃	95	27.3	..	Dark-colored liquid containing suspended material
15	100.0	100.0	0.45 HCl ^g	95	30.3	..	Dark-colored liquid containing suspended material

^a Determined only on soluble fraction or whole.

^b Added as 0.175 gram 60 per cent acid; 60 per cent perchloric acid used in all experiments.

^c Could not be precipitated in water, alcohol, ether, or benzene. Evaporated to sirup in vacuum desiccator over soda lime; then ground and extracted with ether.

^d Washed with alcohol and ether and dried. It swelled in water.

^e Perchloric acid appears to react somewhat with acetic anhydride, giving yellow-green solution.

^f Reaction mixture would not precipitate in ice water, alcohol, or benzene and gave very fine, slowly settling precipitate in ether. Recovered by evaporating reaction mixture in vacuum desiccator over soda lime, dissolving resulting sirup in chloroform, extracting remaining acid and anhydride with water, drying chloroform solution, and evaporating solvent.

^g Added as 2.0 grams 90 per cent acid.

^h Added as 1.2 grams concentrated acid.

Table II. Effect of Varying Catalyst Concentration on Properties of Potato Starch Acetate
(Acetylation Mixture: 50 Grams of Dry Starch, 100 Grams of Glacial Acetic Acid, 100 Grams of Acetic Anhydride. Temperature, 95° C.)

PT. NO.	HClO ₄ Gram	REACTION TIME Hours	ACETYL		Whole %	VISCOSITY Centistokes ^a	FINAL REACTION MIXTURE
			Soluble fraction %	Insoluble fraction %			
1	0.0350	9.75	43.6	5.4 ^b	..	5.4	Only small amount of solid dissolved
2	0.0673	9.75	42.8	20.9 ^b	..	40.0	Only small amount of solid dissolved
3	0.1050	9	43.8	62.4	Translucent, viscous, amber-colored liquid
4	0.1544	9	44.8 ^c	3.6	Somewhat darker and thinner than No. 3
5	0.1910	9	46.9 ^c	2.0	Dark-colored, mobile solution
6	0.2264	9	49.4 ^c	1.7	Very dark, mobile solution

^a Determined on either soluble fraction or whole.

^b Acetic acid and anhydride extracted with petroleum ether.

^c Acid and anhydride distilled off with toluene.

Table III. Results of Acetylation of Potato Starch of Variable Moisture Content in Acetic Anhydride-Glacial Acetic Acid Mixtures

(Catalyst, 0.105 Gram of Perchloric Acid; Time, 9 Hours. 50 Grams of Dry Starch or Equivalent Used)

EXPT. NO.	ACETIC ACID Grams	ACETIC ANHYDRIDE Grams	MOISTURE IN STARCH %	ACETYL %	VISCOSITY Centistokes
1	100.0	100.0	0.0	43.8	62.4
2	83.3	114.2	5.0	43.2	49.2
3	63.3	131.2	9.9	43.1	142.9
4	40.0	151.0	14.8	42.6	157.9
5	17.5	170.5	20.0	43.3	296.9

initial mixture of starch suspended in the acetic anhydride-acetic acid medium. As acetylation begins, the starch acetate produced becomes colloiddally dispersed or dissolves in the reaction medium. Clear solutions of starch acetate in the reaction medium are obtained when the concentration is not too high and after a certain amount of degradation has occurred.

Samples withdrawn at intervals from an acetylation mixture were examined to determine changes in acetyl value and in composition. Table IV shows the progressive changes in amount of acetyl and in viscosity of successive samples of starch acetate removed. The viscosity of samples recovered by both the ether and water methods increased regularly as the degree of acetylation increased. For the most part, ether-recovered samples were higher in viscosity than water-recovered samples. Maximum viscosity was reached in 10 hours, after which the viscosity decreased slightly during the next hour. This may have been caused by molecular degradation, although the acetyl continued to increase slightly.

The solubility of starch acetate depends principally on the degree of substitution and extent of degradation. Lowly acetylated starch having an acetyl content ranging from approximately 5 to 15 per cent is dispersible or soluble in water if the water is sufficiently degraded. Lowly acetylated, degraded samples are frequently soluble in alcohol also. Starch acetate of approximately 30 per cent acetyl or more soluble in organic solvents, the extent solubility again being dependent a great deal upon extent of degradation. Pyridine and ethylene chlorohydrin are among the best solvents for starch acetates, including those with 30 to 40 per cent acetyl. With higher substitution (40 to 44.8 per

Table IV. Recovery of Starch Acetate from Reaction Solution by Ether Extraction as Compared with Aqueous Precipitation

(Reaction Mixture: 300 Grams of Dry Potato Starch, 600 Grams of Glacial Acetic Anhydride. Catalyst, 0.63 Gram of Perchloric Acid. Temperature, 95° C.)

SAMPLE NO.	REACTION TIME Min.	ACETYL		VISCOSITY ^a	
		Ether %	Water %	Ether Centistokes	Water Centistokes
1	30	1.8	1.7
2 ^b	120	4.1	4.6
2 ^c	120	33.6	40.0	Not run	3.1
3 ^b	180	7.2	9.8
3 ^c	180	44.5	45.8	6.7	5.2
4	240	32.5	36.4	7.5	9.2
5	300	37.7	39.7	21.6	21.4
6	360	39.3	41.5	46.0	30.2
7	400	41.2	42.2	48.4	38.2
8	430	41.6	42.6	64.9	40.6
9	550	42.5	43.7	76.9	52.3
10	610	43.0	43.7	99.6	53.9
11	675	43.1	43.9	69.1	53.3

^a Determined on either soluble fraction or whole.

^b Sample recovered from undissolved solids.

^c Sample recovered from soluble portion.

cent acetyl), starch acetates become soluble in acetone, chloroform, ethyl acetyl glycolate, hydroxyethyl acetate, ethylene glycol monobenzyl ether, ethylene chloride, tetrachloroethane, methyl carbitol, and certain of the nitroparaffins and their

derivatives, such as nitromethane, nitroethane, 1-nitropropane, 1-amino-2-methyl-1-propanol, and 2-nitro-1-butanol.

Fractions of samples 2 and 3 which were soluble in the reaction mixture were also soluble in pyridine, ethylene chlorohydrin, chloroform, and acetone. Beginning with sample 4 and continuing thereafter, the product as a whole became increasingly soluble in pyridine, then in ethylene chlorohydrin, chloroform, and finally in acetone.

Microscopic examination of samples of Table IV showed a gradual decrease in number of starch granules per drop of acetylation mixture spread on a slide. Only a few granules remained at the time observations were stopped after about 11 hours of acetylation.

Acetylations of potato starch by Methods I and II could be carried out so as to reproduce acetyl values rather closely. The viscosity of the solutions of the starch acetate, however, showed more variation. This is not surprising in view of the facts that aqueous pastes made from the same variety and source of starch show considerable variation in viscosity and that even in simple acid conversions of starch viscosity reduction is not strictly reproducible.

Most acetylations of starch by Method I were interrupted at the end of 9 hours, when acetylation was essentially complete under optimum conditions. When observations were made well beyond 9 hours (Table V), degradation was indicated by the gradual decrease in viscosity and increased solubility range. The time at which the mixture reached 95° C. was taken as zero time. This corresponded to approximately one hour after the constituents were mixed.

Practically the same percentage of acetyl was obtained for corresponding samples given in Table V, recovered by aqueous precipitation and by toluene extraction. Viscosities were also nearly the same.

Optical rotation measurements made on samples given in Tables V and XI and on a number of other samples not recorded gave no simple relationship between the specific rotation and the corresponding acetyl value. Similarly, no relationship was found between the specific rotation and viscosity. Samples prepared by the

Table V. Changes Accompanying Extended Treatment in Reaction Mixture
(Composition: 300 Grams of Dry Potato Starch, 600 Grams of Glacial Acetic Acid, 600 Grams of Acetic Anhydride. Catalyst, 0.63 Gram of Perchloric Acid. Temperature, 95° C.)

SAMPLE NO.	REACTION TIME Hours	ACETYL		VISCOSITY ^a		SPECIFIC ROTATION IN PYRIDINE, 10% SOLUTION [α] _D ²⁵
		Toluene %	Water %	Toluene Centistokes	Water Centistokes	
1	0	..	1.2 ^b
2	2	..	47.9 ^c
			3.6 ^b		3.2	
3	8.5	43.0	44.0	28.8	28.1	163.9
4	12	44.3	44.7	28.2	24.7	168.8
5	19	44.2	44.2	17.8	18.6	158.5
6	34.5	44.6	43.7	12.1	13.0	157.9
7	43	44.6	42.2	10.2	10.8	160.4

^a Determined on either soluble fraction or whole.

^b Portion of sample insoluble in reaction medium.

^c Portion of sample soluble in reaction medium. Would not precipitate in cold water; precipitated and washed in absolute alcohol.

same method and agreeing closely in percentage of acetyl and viscosity often gave divergent specific rotation values, falling in general between the extremes given in Tables V and XI.

Comparative acetylations were carried out on different varieties of starch under the optimum conditions for potato starch. As shown in Table VI, tapioca, wheat, and sweet potato starches acetylated at rates comparable with that of potato starch. Cornstarch acetylated faster than potato starch. Potato starch acetate had the highest viscosity of all the varieties prepared. The highest grade commercial starch obtainable in each variety was used. Optimum conditions were not determined for starches other than potato, but apparently they differ with each variety of starch.

Table VI. Acetylation of Different Varieties of Starch

(Acetylation Mixture: 50 Grams of Dry Starch, 100 Grams of Acetic Anhydride, 100 Grams of Glacial Acetic Acid, 0.105 Gram of Perchloric Acid. Temperature, 95° C. Time, 9 Hours)

EXPT. No.	STARCH	ACETYL %	VISCOSITY Centistokes
1	Potato	43.8	62.4
2	Wheat	44.1	3.7
3	Sweet potato	41.3	16.2
4	Tapioca	43.2	2.8
5	Corn	47.1	3.8
6	Rice	44.1	35.9

METHOD II. Dry starch was swelled in 90 per cent formic acid prior to acetylation. The starch swelled rapidly in its own weight of acid, which was the pretreatment mixture in the authors' experiments, although the ratio of acid to starch could be reduced to as low as 0.5 part acid to 1 part starch, and still result in swelling the starch.

Tests showed that only a small amount of the formyl radical was substituted into the starch (or the starch acetate) under the conditions of pretreatment. Dry starch swelled in an equal weight of anhydrous formic acid and then freed of the acid by treatment in a vacuum desiccator over soda lime contained approximately 2 per cent combined formyl. Formyl content of the starch acetate (approximately 1 per cent of the weight of the acetate) was obtained by saponifying the ester, acidifying with phosphoric acid, distilling the fatty acids under reduced pressure, and determining formic acid (1).

In these experiments, the swelled starch was immediately added to the acetylation liquid without removal of the formic acid. Starch in the freshly swollen condition acetylated more readily than after removing the formic acid. The free formic acid, however, was decomposed into carbon monoxide and water by the action of acetic anhydride. This reaction, which has been noted by others (14, 21), proceeded very slowly at room temperature but rapidly at 95° C.

Starch swelled in formic acid, unlike the original starch, acetylated better in acetic anhydride than in a mixture of an-

Table VII. Acetylation of Preswelled Starch in Glacial Acetic Acid, Acetic Anhydride, and Mixtures

(50 Grams of Dry Potato Starch Swelled in 50 Grams of 90% Formic Acid at Room Temperature. Reaction Temperature, 95° C.)

EXPT. No.	ACETIC ACID Grams	ACETIC ANHYDRIDE Grams	CATALYST Gram	TIME Hours	ACETYL %
1	270	None	0.105 HClO ₄ ^a	3 ^b	17.3
2	135	135	0.105 HClO ₄ ^a	9 ^b	19.6
				1 ^c	10.7
				2 ^c	26.6
				4 ^c	28.5
				5 ^c	29.6
				10	38.5
3	None	270	0.105 HClO ₄ ^a	1 ^{1/2} ^{c,d}	17.4
				1 ^{1/2} ^c	29.1
				3 ^{1/4} ^c	38.3
				1	39.1
				1 ^{1/2}	43.8
				2	45.1
				5 ^{1/4}	45.9
4	None	270	None	3	33.3

^a Added as 0.175 gram of 60 per cent HClO₄.

^b Reaction mixture would not precipitate in ice water; recovered by precipitating and washing in ether.

^c Reaction mass precipitated in ice water in a white gelatinous mass; ester separated and dehydrated with alcohol.

^d Reaction vessel placed in bath at 25° C. Stirring and timing began immediately. Reaction mass warmed gradually to 95° C. in one hour.

hydride and acid. Acetic acid alone acetylated the swelled starch slowly. Table VII shows the differences found in acetylating swelled starch in acetic acid, acetic anhydride, and a mixture of the two. The products of experiments 2 and 3 were sampled at intervals in order to gain some insight into the rate of acetylation. The catalytic acetylation of formic acid-swelled starch in acetic anhydride was so rapid that reproducible data were difficult to obtain. Experiment 3, however, is typical and representative. Acetyl content equivalent to complete substitution of starch was reached in 1 hour at 95° C., corresponding to 2 hours after the mixture had been placed in the bath at 25° C.

Either perchloric or sulfuric acid was used to catalyze the acetylation of formic acid-swelled starch. Both were effective in promoting esterification and did not degrade the starch to any great extent in the concentrations used.

Table VIII shows that complete acetylation of formic acid-swelled starch was readily obtained with sulfuric acid as catalyst in 3 hours at 75° C., although the product was rather insoluble in the usual organic solvents unless treated for a period longer than 3 hours. Both samples 1 and 2, run for 3 hours at 75° and 95° C., respectively, were too insoluble in pyridine to prepare solutions more concentrated than 1 per cent. Nine hours' treatment at either 75° or 85° C., on the other hand, gave preparations soluble enough for vis-

cosity determination on 10 per cent solutions. Samples 1, 2, and 3 gave clear, viscous solutions in tetrachloroethane and ethylene chlorohydrin and were partly soluble in chloroform and insoluble in acetone. Sample 4 was soluble in tetrachloroethane, ethylene chlorohydrin, and chloroform, but insoluble in acetone.

Table VIII. Acetylation of Preswelled Starch in Acetic Anhydride

(Composition: 50 Grams of Dry Potato Starch Swelled in 50 Grams of 90% Formic Acid at Room Temperature; 270 Grams of Acetic Anhydride Catalyst, 0.29 Gram of Sulfuric Acid)

EXPT. No.	TEMPERATURE ° C.	TIME Hours	ACETYL %	VISCOSITY Centistokes
1	75	3	45.5	3.3 ^a
2	95	3	45.7	2.8 ^a
3	75	9	45.0	365.7
4	85	9	45.3	173.7

^a One per cent solution in pyridine.

Table IX shows the effect of variation of catalyst concentration on the character of the acetylated starch. A small amount of concentrated sulfuric acid as catalyst, 0.1 part per 50 parts of starch in 270 parts of acetic anhydride, was sufficient to give nearly complete acetylation in 1 hour at 95° C. The product of acetylation became more soluble in pyridine as increasing amounts of catalyst were employed, and degradation was more pronounced, as indicated by viscosity measurements.

When perchloric acid is used as catalyst for the acetylation of formic acid-swelled

Table IX. Effect of Catalyst Concentration on Acetylation of Preswelled Starch

(Composition: 50 Grams of Dry Potato Starch Swelled in 50 Grams of 90% Formic Acid; 270 Grams Acetic Anhydride. Catalyst, Sulfuric Acid. Temperature, 95° C.)

EXPT. No.	CATALYST Gram	TIME Hours	ACETYL %	VISCOSITY Centistokes	FINAL REACTION MIXTURE
1	0.0	3	33.3	.. ^a	Thick, white paste
2	0.1	1	42.7	.. ^a	Viscous, translucent, white mass
		3	45.2	.. ^a	
3	0.3	3	45.6	.. ^a	Viscous, translucent, white mass
4	0.4	1	43.5	19.3	Light-brown, clear, mobile liquid
		3	46.1	9.3	
5	0.6	1	47.3	7.9	Light-brown, clear, mobile liquid
		3	48.9	4.6	

^a Solubility insufficient to permit viscosity determination.

starch in acetic anhydride, the catalyst can be added in one step at the beginning and the mixture subsequently warmed slowly to the reaction temperature. With

uric acid as catalyst, ebullition of the acetylation mass caused by evolution of carbon monoxide is more easily controlled by gradual addition of the catalyst. Table X shows that addition of the sulfuric acid over about 90 minutes rather than in one step gave rapid acetylation even with a low catalyst concentration in the earlier part of the experiment.

In order to follow degradative changes taking place during extended treatment of starch acetate in the acetylation mixture of Method II, a larger scale experiment was run for 20 hours and sampled at intervals. All the catalyst was added at the beginning. The mixture was allowed to stand for 2 hours without application of external heat, and then the reaction vessel was placed directly in a bath at 95° C. The data in Table XI, which were taken on samples from this larger experimental run, show that acetylation was more than 90 per cent complete at the time the batch was placed in the bath at 95° C. Failure to reach the theoretical value for complete acetylation was probably due to the fact that the agitation was not vigorous enough to disintegrate small lumps of partly acetylated starch. The first sample recovered, although high in viscosity, gave a perfectly clear solution in pyridine. Viscosity decreased rapidly during the first hour's treatment at 95° C. and later at a diminishing rate.

Table X. Acetylation of Preswelled Starch, Stepwise Addition of Catalyst

(Composition: 50 Grams of Dry Potato Starch Swelled in 50 Grams of 90% Formic Acid; 270 Grams of Acetic Anhydride. Catalyst, 0.03 to 0.3 Gram of Sulfuric Acid; Approximate Weight per Drop, 0.03 Gram)

SAMPLE No.	TIME Min.	TEMPERATURE ° C.	TOTAL H ₂ SO ₄ PRESENT Drops	ACETYL %
0 ^a	0	25	1	..
1 ^a	15	50	2	..
2	30	68	3	13.1
3	45	82	4	20.4
4	60	95	5	34.4
.. ^b	70	95	7	..
.. ^b	80	95	9	..
5	90	95	9	42.7
6	120	95	9	46.0
7	315	95	9	47.0

^a Sample swelled and partly dissolved in ice water; not analyzed.
^b No sample taken.

Table XI. Changes Accompanying Extended Treatment in Reaction Mixture

(Composition: 200 Grams of Dry Potato Starch Swelled in 200 Grams of 90% Formic Acid; 1,080 Grams of Acetic Anhydride. Catalyst, 1.16 Grams of Concentrated Sulfuric Acid)

TIME AT 95° C. hrs	ACETYL %	VISCOSITY Centistokes	SPECIFIC ROTATION IN PYRIDINE, 10% SOLUTION [α] _D ²⁵
0	41.6	862.3	176.2
1	43.5	49.4	170.1
2	42.7	40.2	173.1
3	44.1	28.7	169.3
20	44.1	8.2	165.8

Starch acetates of higher viscosity were obtained by Method II than by Method I because of less degradation. The least degraded triacetates prepared by Method II, however, were practically insoluble in a variety of solvents tried—e.g., acetone, chloroform, tetrachloroethane, and ethylene chloride. Pyridine was used in preparing solutions for viscosity determination. The least degraded starch acetates did not form true solutions in pyridine but contained transparent gelled lumps in suspension. These colloidal solutions were prepared for viscosity measurement by running them through a hand-operated homogenizer until smooth and then filtering them through glass wool to remove any remaining insoluble particles. Viscosity measurements on the resulting "solutions" served as an index to the degree of degradation.

As Table XII shows, the preparations made by Method II, represented by starch acetates 1 and 2, were much more viscous than the commercial low-viscosity cellulose acetate but less viscous than high-viscosity cellulose acetate. Comparison of the samples was made with 10 per cent pyridine solutions of the esters. Starch acetate 3, representative of the higher viscosity starch acetates produced by Method I, was considerably more viscous than the commercial low-viscosity cellulose acetate. Starch acetates 4 and 5, typical of the less degraded preparations made by Method II, were compared with the commercial high-viscosity cellulose acetate in 1 per cent concentration because of the low solubility of the former. The viscosity of starch acetate 1 was determined also in 1 per cent concentration to permit comparison with that of the 10 per cent concentration.

Table XII. Viscosity of Starch Acetate and Commercial Cellulose Acetate in Pyridine Solutions

SAMPLE DESIGNATION	CONCENTRATION %	VISCOSITY Centistokes
Commercial cellulose acetate 1 ^a (37.5% acetyl)	10	1,019.5
Commercial cellulose acetate 2 ^b (39.5% acetyl)		131.2
Starch acetate 1 (38.8% acetyl) ^c		961.4
Starch acetate 2 (41.6% acetyl) ^c		862.3
Starch acetate 3 (43.3% acetyl) ^d		296.9
Commercial cellulose acetate 1	1	3.5
Starch acetate 4 (45.5% acetyl) ^c		3.3
Starch acetate 1		2.8
Starch acetate 5 (45.0% acetyl) ^c		3.0
Commercial cellulose acetate 2		3.0

^a Designated by manufacturer as "high-viscosity cellulose acetate".
^b Designated by manufacturer as "low-viscosity cellulose acetate".

^c Prepared by Method II.
^d Prepared by Method I.

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Summary and Conclusions

Optimum conditions for acetylating potato starch by two methods were determined: composition of acetylating medium, temperature, catalyst concentration, and reaction time.

Method I required longer time and produced acetates of a greater degree of degradation than Method II.

In the second method, the use of oven-dried starch and 90 per cent commercially available formic acid was preferred to the use of air-dry starch and nearly anhydrous formic acid. A small amount of formyl was present in starch acetate prepared by Method II.

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